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Dielectric Theory on the Interfacial Polarization for Two-Phase Mixtures

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Theoretical considerations are made on the interfacial polarization for two-phase mixtures, especially for spherical dispersions.

The general solutions of the Maxwell and the Wagner theory are derived, showing that the dielectric dispersion due to the interfacial polarization is characterized by a single relaxation time.

A new theory of the interfacial polarization is developed on the assumption that the Wagner equation holds for an infinitesimally increasing process in concentration of the dispersion system.

Both the Wagner and the new theory are able to interpret considerable changes in the dielectric properties on phase inversion of emulsions.

Numerical considerations of the theoretical formulas are given for some cases of practical interest. The Maxwell theory is of no use for spherical dispersion systems, though this theory may be valid for two-phase mixtures in a stratified structure. The Wagner theory is valid qualitatively for usual emulsions, being of no use for nitrobenzene-in-water emulsions. The new theory is valid not only for usual emulsions but also for nitrobenzene-in-water emulsions. From the numerical considerations, it is elucidated that the magnitude of the dielectric dispersion depends strongly on the relationship among dielectric constants and conductivities of the dispersion medium and the disperse phase.

List of Symbols

ε , κ , ε^* , κ^* , γ : the dielectric constant, the electrical conductivity, the complex dielectric constant, the complex conductivity and the imaginary part of the complex dielectric constant† of the dispersion system respectively. Symbols with the subscript m or p such as ε_m , κ_m , ε_m^* , κ_m^* , and γ_m or ε_p , κ_p , ε_p^* , κ_p^* , and γ_p , refer to the continuous medium or to the disperse phase respectively.

The following relations hold among the above quantities:

$$\varepsilon^* = \frac{q}{j\omega} \kappa^* = \varepsilon + \frac{q}{j\omega} \kappa = \varepsilon - j\gamma, \quad (1)$$

$$\varepsilon_m^* = \frac{q}{j\omega} \kappa_m^* = \varepsilon_m + \frac{q}{j\omega} \kappa_m = \varepsilon_m - j\gamma_m \quad (2)$$

and

$$\varepsilon_p^* = \frac{q}{j\omega} \kappa_p^* = \varepsilon_p + \frac{q}{j\omega} \kappa_p = \varepsilon_p - j\gamma_p, \quad (3)$$

where ω is the angular frequency, $j = \sqrt{-1}$, numerical factor $q = 112.94 \times 10^{11}$ and

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† The imaginary part $\frac{q}{\omega} \kappa$ of the complex dielectric constant is usually denoted by ε'' . In this paper a symbol γ is used instead of ε'' in order to avoid confusions in complicated expressions.

the conductivities are expressed in Ω/cm units.

Φ : the volume fraction of the disperse phase.

$\varepsilon_h, \varepsilon_l$: the limiting values of ε at higher and lower frequencies respectively.

κ_h, κ_l : the limiting values of κ at higher and lower frequencies respectively.

τ : the relaxation time of a dielectric dispersion.

1. INTRODUCTION

It is known theoretically as well as experimentally that a heterogeneous structure of material gives rise to a dielectric dispersion, which is so-called interfacial polarization.

A possibility of the dielectric dispersion caused by a heterogeneous structure of dielectrics was first pointed out theoretically by Maxwell¹⁾ by means of a stratified model. In the case of heterogeneous mixtures of spherical particles, this stratified model is practically of no use, since the distinction between the dispersion medium and the disperse phase is left out of consideration in this model.

Wagner²⁾ proposed a theory of the interfacial polarization for a sparsely distributed dispersion of spherical particles, and showed a solution of his equation only for a special case of lower concentrations and the non-conductive medium. Afterwards the Wagner theory was extended to an ellipsoidal dispersion by Sillars³⁾ and Fricke.⁴⁾

On the other hand, several investigators observed dielectric dispersions due to the interfacial polarization in water-in-oil (W/O) type emulsions.

In earlier studies Sillars³⁾ found the dielectric loss tangent due to the interfacial polarization for emulsions of water in wax, concentrations of the internal phase being less than 7% by volume. His results did not agree with the theoretical prediction given by Wagner.

Hamon⁵⁾ measured the dielectric loss factors of mixtures of spherical particles of an organic semiconductor (copper phthalocyanine) in paraffin wax, and obtained reasonably good agreement with the Wagner theory, volume concentrations of the internal phase being less than 3%.

Kharadly and Jackson⁶⁾ observed dielectric dispersions due to the interfacial polarization for emulsions of polystyrene and nitrobenzene in the mixture of paraffin wax and polythene at concentrations up to 46%. Their theoretical analysis, which is similar to the Wagner theory, failed to account for the experimental results of the emulsions at concentrations above 20%.

Recently Dryden and Meakins⁷⁾ have reported the dielectric absorption of the Maxwell-Wagner type for water-in-wool wax emulsions, concentrations being less than 38%. Their results are insufficient for rigorous considerations of the interfacial polarization, since they gave no data on the real part of the dielectric constant.

More recently the author⁸⁾ have measured the dielectric constants and the conductivities of water-in-nujol emulsions over a wide range of concentration up to 80% and at frequencies ranging from 20cps. to 5mc. In his measurements, striking dielectric dispersions due to the interfacial polarization were observed at high frequency range above 100kc., the limiting dielectric constants at high fre-

quencies being expressed well by the equation of the Bruggeman type⁹⁾ over the whole range of concentration.

On the contrary, few papers have been reported on the dielectric study of oil-in-water (O/W) type emulsions.

In the previous investigations,^{10,11)} the dielectric constants and conductivities of nujol and carbon tetrachloride-in-water emulsions were measured for high concentrations up to 85%, and no dielectric dispersion due to the interfacial polarization could be observed over a frequency range of 20 cps. to 3mc. The observed dielectric constants and conductivities of these O/W emulsions did not agree with the Wiener equation, which is a special case of the Wagner theory, and were expressed better by the equation of the Bruggeman type⁹⁾ over the whole range of concentration.

Up to the present, dielectric dispersions due to the interfacial polarization have been observed only in the W/O type emulsions as mentioned above, and no example of the interfacial polarization has been found in the O/W type yet.

It should also be noted for characteristics of dispersion systems that O/W emulsions show different dielectric constants and conductivities from those of the W/O type with the same volume fraction of the oil. In practice, these characteristics are often utilized as a crude measure of the determination of emulsion type and the detection of phase inversion.¹²⁾

Although the interfacial polarization is of practical interest especially in concentrated emulsions, it appears to us that its theoretical treatment for a spherical dispersion has not been developed beyond the Wagner theory.

In the present paper, the author has intended to deal with the theories on the interfacial polarization for two-phase mixtures, especially for spherical dispersions. First the solution of the Maxwell theory is discussed. Next the general solution of the Wagner theory is derived, and is applied to some cases of emulsions. Thirdly a new theory of the interfacial polarization is developed, and is applied to the practical cases of emulsions. Finally the results of these theories are discussed quantitatively for some cases of practical interest.

2. MAXWELL THEORY

A) Solution of the Maxwell Equation

Maxwell¹³⁾ explained the dielectric dispersion due to the interfacial polarization of a heterogeneous system by means of a stratified model. He obtained the complex dielectric constant ϵ^* and the complex conductivity κ^* for a heterogeneous system in the stratified structure as follows:

$$\frac{1}{\epsilon^*} = \frac{1}{\epsilon_m^*}(1-\Phi) + \frac{1}{\epsilon_p^*}\Phi \quad (4)$$

and

$$\frac{1}{\kappa^*} = \frac{1}{\kappa_m^*}(1-\Phi) + \frac{1}{\kappa_p^*}\Phi. \quad (5)$$

Rearranging, we have

$$\varepsilon^* = \varepsilon_m^* \frac{\varepsilon_p^*}{\varepsilon_p^* + \Phi(\varepsilon_m^* - \varepsilon_p^*)} \quad (6)$$

and

$$\kappa^* = \kappa_m^* \frac{\kappa_p^*}{\kappa_p^* + \Phi(\kappa_m^* - \kappa_p^*)}. \quad (7)$$

Inserting Eqs. (1),(2) and (3) into Eq. (6), we have

$$\varepsilon^* = \left(\varepsilon_m + \frac{q}{j\omega} \kappa_m \right) \frac{\varepsilon_p + \frac{q}{j\omega} \kappa_p}{\left[\varepsilon_p + \Phi(\varepsilon_m - \varepsilon_p) \right] + \frac{q}{j\omega} \left[\kappa_p + \Phi(\kappa_m - \kappa_p) \right]}. \quad (8)$$

If we put

$$\left. \begin{aligned} A &= \varepsilon_m \\ B &= q\kappa_m \\ C &= \varepsilon_p \\ D &= q\kappa_p \\ J &= \varepsilon_p + \Phi(\varepsilon_m - \varepsilon_p) \\ K &= q[\kappa_p + \Phi(\kappa_m - \kappa_p)], \end{aligned} \right\} \quad (9)$$

Eq. (8) is transformed to

$$\varepsilon^* = \left(A + \frac{B}{j\omega} \right) \frac{C + \frac{D}{j\omega}}{J + \frac{K}{j\omega}}, \quad (10)$$

$$= \frac{AD + BC + j\omega AC + \frac{1}{j\omega} BD}{K + j\omega J}, \quad (11)$$

$$= \frac{AC}{J} + \frac{\frac{AD+BC}{K} - \frac{BDJ}{K^2} - \frac{AC}{J}}{1 + j\omega \frac{J}{K}} + \frac{1}{j\omega} \cdot \frac{BD}{K}, \quad (12)$$

$$= \frac{AC}{J} + \frac{(AK - BJ)(DJ - CK)}{JK^2} \frac{1}{1 + j\omega \frac{J}{K}} + \frac{1}{j\omega} \cdot \frac{BD}{K}. \quad (13)$$

Hence Eq. (8) is rewritten in a simplified form:

$$\varepsilon^* = \varepsilon_h + \frac{\varepsilon_l - \varepsilon_h}{1 + j\omega\tau} + \frac{q}{j\omega} \kappa_l, \quad (14)$$

where

$$\varepsilon_h = \frac{AC}{J} = \varepsilon_m \frac{\varepsilon_p}{\varepsilon_p + \Phi(\varepsilon_m - \varepsilon_p)}, \quad (15)$$

$$\begin{aligned} \varepsilon_l &= \frac{AD+BC}{K} - \frac{BDJ}{K^2} \\ &= \frac{\varepsilon_m \kappa_p^2 + \Phi(\varepsilon_p \kappa_m^2 - \varepsilon_m \kappa_p^2)}{[\kappa_p + \Phi(\kappa_m - \kappa_p)]^2}, \end{aligned} \quad (16)$$

$$= \varepsilon_m \frac{\kappa_l}{\kappa_m} + \frac{(\varepsilon_p \kappa_m - \varepsilon_m \kappa_p) \kappa_m \Phi}{[\kappa_p + \Phi(\kappa_m - \kappa_p)]^2}, \quad (17)$$

$$\begin{aligned}\varepsilon_l - \varepsilon_h &= \frac{(AK - BJ)(DJ - CK)}{JK^2} \\ &= \frac{(\varepsilon_m \kappa_p - \varepsilon_p \kappa_m)^2 \Phi (1 - \Phi)}{[\varepsilon_p + \Phi(\varepsilon_m - \varepsilon_p)][\kappa_p + \Phi(\kappa_m - \kappa_p)]^2},\end{aligned}\quad (18)$$

and

$$\tau = \frac{J}{K} = \frac{\varepsilon_p + \Phi(\varepsilon_m - \varepsilon_p)}{\kappa_p + \Phi(\kappa_m - \kappa_p)} \cdot \frac{1}{q}. \quad (19)$$

In a similar manner we obtain

$$\kappa^* = \kappa_l + \frac{j\omega\tau(\kappa_h - \kappa_l)}{1 + j\omega\tau} + \frac{j\omega}{q} \varepsilon_h, \quad (20)$$

in which

$$\kappa_l = \frac{BD}{qK} = \kappa_m \frac{\kappa_p}{\kappa_p + \Phi(\kappa_m - \kappa_p)}, \quad (21)$$

$$\begin{aligned}\kappa_h &= \frac{1}{q} \left[\frac{AD + BC}{J} - \frac{ACK}{J^2} \right] \\ &= \frac{\kappa_m \varepsilon_p^2 + \Phi(\kappa_p \varepsilon_m^2 - \kappa_m \varepsilon_p^2)}{[\varepsilon_p + \Phi(\varepsilon_m - \varepsilon_p)]^2},\end{aligned}\quad (22)$$

$$= \kappa_m \frac{\varepsilon_h}{\varepsilon_m} + \frac{(\kappa_p \varepsilon_m - \kappa_m \varepsilon_p) \varepsilon_m \Phi}{[\varepsilon_p + \Phi(\varepsilon_m - \varepsilon_p)]^2}, \quad (23)$$

$$\begin{aligned}\kappa_h - \kappa_l &= \frac{1}{q} \left[\frac{(AK - BJ)(DJ - CK)}{KJ^2} \right] \\ &= \frac{(\varepsilon_m \kappa_p - \varepsilon_p \kappa_m)^2 \Phi (1 - \Phi)}{[\kappa_p + \Phi(\kappa_m - \kappa_p)][\varepsilon_p + \Phi(\varepsilon_m - \varepsilon_p)]^2},\end{aligned}\quad (24)$$

and

$$(\kappa_h - \kappa_l)\tau q = \varepsilon_l - \varepsilon_h. \quad (25)$$

From Eqs. (14) and (18) it is easily seen that a dielectric dispersion characterized by a single relaxation time arises when $\varepsilon_m \kappa_p \neq \varepsilon_p \kappa_m$. Eq. (15) for the limiting dielectric constant at high frequencies ε_h is the same as one of Wiener's¹³⁾ *Grenzformeln*.

B) Approximation for Special Cases

We shall apply the results of the Maxwell theory to the oil-water emulsions which are of practical interest. Since the conductivity of the water phase is, generally in emulsions, much larger than that of the oil phase, Eqs. (16), (21) and (22) can be simplified as follows:

i) Case $\kappa_m \gg \kappa_p$ (O/W type emulsion)

Here Eqs. (15), (16), (21) and (22) are reduced to the following respectively:

$$\varepsilon_h = \varepsilon_m \frac{\varepsilon_p}{\varepsilon_p + \Phi(\varepsilon_m - \varepsilon_p)}, \quad (26)$$

$$\varepsilon_l = \varepsilon_p \frac{1}{\Phi}, \quad (27)$$

$$\frac{\kappa_l}{\kappa_p} = \frac{1}{\Phi} \quad (28)$$

and

$$\frac{\kappa_h}{\kappa_m} = \left[\frac{\varepsilon_p}{\varepsilon_p + \Phi (\varepsilon_m - \varepsilon_p)} \right]^2 (1 - \Phi). \quad (29)$$

ii) Case $\kappa_p \gg \kappa_m$ (W/O type emulsion)

Here Eqs. (15), (16), (21) and (22) are reduced to the following respectively:

$$\varepsilon_h = \varepsilon_m \frac{\varepsilon_p}{\varepsilon_p + \Phi (\varepsilon_m - \varepsilon_p)}, \quad (30)$$

$$\varepsilon_t = \varepsilon_m \frac{1}{1 - \Phi}, \quad (31)$$

$$\frac{\kappa_t}{\kappa_m} = \frac{1}{1 - \Phi} \quad (32)$$

and

$$\frac{\kappa_h}{\kappa_p} = \left[\frac{\varepsilon_m}{\varepsilon_p + \Phi (\varepsilon_m - \varepsilon_p)} \right]^2 \Phi. \quad (33)$$

3. WAGNER THEORY

A) General Solution of the Wagner Equation

Wagner²⁾ showed that, for a dispersion system where spherical particles are sparsely distributed throughout the dispersion medium, the complex dielectric constant and the complex conductivity of a heterogeneous mixture are given by the following expressions:

$$\frac{\varepsilon^* - \varepsilon_m^*}{\varepsilon^* + 2\varepsilon_m^*} = \frac{\varepsilon_p^* - \varepsilon_m^*}{\varepsilon_p^* + 2\varepsilon_m^*} \Phi \quad (34)$$

and

$$\frac{\kappa^* - \kappa_m^*}{\kappa^* + 2\kappa_m^*} = \frac{\kappa_p^* - \kappa_m^*}{\kappa_p^* + 2\kappa_m^*} \Phi. \quad (35)$$

Rearranging, we have

$$\varepsilon^* = \varepsilon_m^* \frac{2\varepsilon_m^* + \varepsilon_p^* - 2\Phi (\varepsilon_m^* - \varepsilon_p^*)}{2\varepsilon_m^* + \varepsilon_p^* + \Phi (\varepsilon_m^* - \varepsilon_p^*)} \quad (36)$$

and

$$\kappa^* = \kappa_m^* \frac{2\kappa_m^* + \kappa_p^* - 2\Phi (\kappa_m^* - \kappa_p^*)}{2\kappa_m^* + \kappa_p^* + \Phi (\kappa_m^* - \kappa_p^*)}. \quad (37)$$

Eqs. (34) and (35) have hitherto been solved only when $\Phi \ll 1$ and $\kappa_m = 0$. General solutions of these equations are derived as shown below.

Inserting Eqs. (1), (2) and (3) into Eq. (36), we have

$$\varepsilon^* = \left(\varepsilon_m + \frac{q}{j\omega} \kappa_m \right) \frac{[2\varepsilon_m + \varepsilon_p - 2\Phi (\varepsilon_m - \varepsilon_p)] + \frac{q}{j\omega} [2\kappa_m + \kappa_p - 2\Phi (\kappa_m - \kappa_p)]}{[2\varepsilon_m + \varepsilon_p + \Phi (\varepsilon_m - \varepsilon_p)] + \frac{q}{j\omega} [2\kappa_m + \kappa_p + \Phi (\kappa_m - \kappa_p)]}. \quad (38)$$

If we put

$$\left. \begin{aligned} A &= \varepsilon_m \\ B &= q\kappa_m \\ E &= 2\varepsilon_m + \varepsilon_p - 2\Phi(\varepsilon_m - \varepsilon_p) \\ F &= q[2\kappa_m + \kappa_p - 2\Phi(\kappa_m - \kappa_p)] \\ G &= 2\varepsilon_m + \varepsilon_p + \Phi(\varepsilon_m - \varepsilon_p) \\ H &= q[2\kappa_m + \kappa_p + \Phi(\kappa_m - \kappa_p)], \end{aligned} \right\} \quad (39)$$

Eq. (38) is transformed to

$$\varepsilon^* = \left(A + \frac{B}{j\omega} \right) \frac{E + \frac{F}{j\omega}}{G + \frac{H}{j\omega}}, \quad (40)$$

$$= \frac{AF + BE + j\omega AE + \frac{1}{j\omega} BF}{H + j\omega G}, \quad (41)$$

$$= \frac{\frac{AE}{G} + \frac{AF + BE}{H} - \frac{BFG}{H^2} - \frac{AE}{G}}{1 + j\omega \frac{G}{H}} + \frac{1}{j\omega} \cdot \frac{BF}{H} \quad (42)$$

Hence Eq. (38) is rewritten in a simplified form:

$$\varepsilon^* = \varepsilon_h + \frac{\varepsilon_l - \varepsilon_h}{1 + j\omega\tau} + \frac{q}{j\omega} \kappa_l, \quad (43)$$

where

$$\varepsilon_h = \frac{AE}{G} = \varepsilon_m \frac{2\varepsilon_m + \varepsilon_p - 2\Phi(\varepsilon_m - \varepsilon_p)}{2\varepsilon_m + \varepsilon_p + \Phi(\varepsilon_m - \varepsilon_p)}, \quad (44)$$

$$\begin{aligned} \varepsilon_l &= \frac{AF + BE}{H} - \frac{BFG}{H^2} \\ &= \frac{\varepsilon_m(2\kappa_m + \kappa_p)^2 + [(9\varepsilon_p - 2\varepsilon_m)\kappa_m^2 - 8\varepsilon_m\kappa_m\kappa_p + \varepsilon_m\kappa_p^2]\Phi - 2\varepsilon_m(\kappa_m - \kappa_p)^2\Phi^2}{[2\kappa_m + \kappa_p + \Phi(\kappa_m - \kappa_p)]^2}, \end{aligned} \quad (45)$$

$$= \varepsilon_m \frac{\kappa_l}{\kappa_m} + \frac{9(\varepsilon_p\kappa_m - \varepsilon_m\kappa_p)\kappa_m\Phi}{[2\kappa_m + \kappa_p + \Phi(\kappa_m - \kappa_p)]^2}, \quad (46)$$

$$\begin{aligned} \varepsilon_l - \varepsilon_h &= \frac{(AH - BG)(FG - EH)}{GH^2} \\ &= \frac{9(\varepsilon_m\kappa_p - \varepsilon_p\kappa_m)^2\Phi(1 - \Phi)}{[2\varepsilon_m + \varepsilon_p + \Phi(\varepsilon_m - \varepsilon_p)][2\kappa_m + \kappa_p + \Phi(\kappa_m - \kappa_p)]^2} \end{aligned} \quad (47)$$

and

$$\tau = \frac{G}{H} = \frac{2\varepsilon_m + \varepsilon_p + \Phi(\varepsilon_m - \varepsilon_p)}{2\kappa_m + \kappa_p + \Phi(\kappa_m - \kappa_p)} \cdot \frac{1}{q}. \quad (48)$$

In a similar manner we obtain

$$\kappa^* = \kappa_l + \frac{j\omega\tau(\kappa_h - \kappa_l)}{1 + j\omega\tau} + \frac{j\omega}{q} \varepsilon_h, \quad (49)$$

in which

$$\kappa_l = \frac{BF}{qH} = \kappa_m \frac{2\kappa_m + \kappa_p - 2\Phi(\kappa_m - \kappa_p)}{2\kappa_m + \kappa_p + \Phi(\kappa_m - \kappa_p)}, \quad (50)$$

$$\begin{aligned}\kappa_h &= \frac{1}{q} \left[\frac{AF+BE}{G} - \frac{AEH}{G^2} \right] \\ &= \frac{\kappa_m(2\varepsilon_m + \varepsilon_p)^2 + [(9\kappa_p - 2\kappa_m)\varepsilon_m^2 - 8\kappa_m\varepsilon_m\varepsilon_p + \kappa_m\varepsilon_p^2]\Phi - 2\kappa_m(\varepsilon_m - \varepsilon_p)^2\Phi^2}{[2\varepsilon_m + \varepsilon_p + \Phi(\varepsilon_m - \varepsilon_p)]^2},\end{aligned}\quad (51)$$

$$= \kappa_m \frac{\varepsilon_h}{\varepsilon_m} + \frac{9(\kappa_p\varepsilon_m - \kappa_m\varepsilon_p)\varepsilon_m\Phi}{[2\varepsilon_m + \varepsilon_p + \Phi(\varepsilon_m - \varepsilon_p)]^2}, \quad (52)$$

$$\begin{aligned}\kappa_h - \kappa_l &= \frac{1}{q} \left[\frac{(AH-BG)(FG-EH)}{HG^2} \right] \\ &= \frac{9(\kappa_m\varepsilon_p - \kappa_p\varepsilon_m)^2\Phi(1-\Phi)}{[2\kappa_m + \kappa_p + \Phi(\kappa_m - \kappa_p)][2\varepsilon_m + \varepsilon_p + \Phi(\varepsilon_m - \varepsilon_p)]^2}\end{aligned}\quad (53)$$

and

$$(\kappa_h - \kappa_l)\tau q = \varepsilon_l - \varepsilon_h. \quad (54)$$

From Eqs. (43) and (47) it is easily seen that a dielectric dispersion characterized by a single relaxation time arises when $\varepsilon_m\kappa_p \approx \varepsilon_p\kappa_m$. Therefore the Cole and Cole plot of Eq. (43) in a complex plane is a semicircular-arc. Eq. (44) for the limiting dielectric constant at high frequencies ε_h is the same as the Wiener equation¹³⁾ of the dielectric constant for a spherical dispersion, and Eq. (50) for κ_l is the same as the equation of the conductivity of dispersion systems used by Fricke.¹⁴⁾

B) Approximation for Special Cases

i) Case $\kappa_m \gg \kappa_p$ (O/W type emulsion)

Here Eqs. (44), (46), (50) and (52) are reduced to the following respectively:

$$\varepsilon_h = \varepsilon_m \frac{2\varepsilon_m + \varepsilon_p - 2\Phi(\varepsilon_m - \varepsilon_p)}{2\varepsilon_m + \varepsilon_p + \Phi(\varepsilon_m - \varepsilon_p)}, \quad (55)$$

$$\begin{aligned}\varepsilon_l &= \varepsilon_m \frac{\kappa_l}{\kappa_m} + \frac{9\varepsilon_p\Phi}{(2+\Phi)^2} \\ &= \varepsilon_m \frac{2(1-\Phi)}{2+\Phi} + \frac{9\varepsilon_p\Phi}{(2+\Phi)^2},\end{aligned}\quad (56)$$

$$\frac{\kappa_l}{\kappa_m} = \frac{2(1-\Phi)}{2+\Phi} \quad (57)$$

and

$$\begin{aligned}\frac{\kappa_h}{\kappa_m} &= \frac{\varepsilon_h}{\varepsilon_m} - \frac{9\varepsilon_m\varepsilon_p\Phi}{[2\varepsilon_m + \varepsilon_p + \Phi(\varepsilon_m - \varepsilon_p)]^2} \\ &= \frac{2\varepsilon_m + \varepsilon_p - 2\Phi(\varepsilon_m - \varepsilon_p)}{2\varepsilon_m + \varepsilon_p + \Phi(\varepsilon_m - \varepsilon_p)} - \frac{9\varepsilon_m\varepsilon_p\Phi}{[2\varepsilon_m + \varepsilon_p + \Phi(\varepsilon_m - \varepsilon_p)]^2}.\end{aligned}\quad (58)$$

ii) Case $\kappa_p \gg \kappa_m$ (W/O type emulsion)

Here Eqs. (44), (46), (50) and (52) are reduced to the following respectively:

$$\varepsilon_h = \varepsilon_m \frac{2\varepsilon_m + \varepsilon_p - 2\Phi(\varepsilon_m - \varepsilon_p)}{2\varepsilon_m + \varepsilon_p + \Phi(\varepsilon_m - \varepsilon_p)}, \quad (59)$$

$$\varepsilon_l = \varepsilon_m \frac{\kappa_l}{\kappa_m} = \varepsilon_m \frac{1+2\Phi}{1-\Phi}, \quad (60)$$

$$\frac{\kappa_l}{\kappa_m} = \frac{1+2\Phi}{1-\Phi} \quad (61)$$

and

$$\frac{\kappa_h}{\kappa_p} = \left[\frac{3\varepsilon_m}{2\varepsilon_m + \varepsilon_p + \Phi(\varepsilon_m - \varepsilon_p)} \right]^2 \Phi. \quad (62)$$

4. NEW THEORY OF THE INTERFACIAL POLARIZATION

A) Derivation of the Basic Equation

The Wagner theory may not hold for the concentrated dispersions, since this theory was derived for a dilute dispersion system.

Now we assume that the Wagner relation (34) holds for the infinitesimal process such that an infinitesimally small quantity of the disperse phase is added to the dispersion system. Namely, for such an infinitesimally additional process, ε_m^* , ε^* and Φ in Eq. (34) should be replaced as follows:

$$\varepsilon_m^* \rightarrow \varepsilon^*, \quad \varepsilon^* \rightarrow \varepsilon^* + \Delta\varepsilon^*, \quad \Phi \rightarrow \frac{\Delta\Phi'}{1-\Phi'}, \quad \dagger$$

where $\Delta\varepsilon^*$ denotes an increment of ε^* associated with an infinitesimal addition of the disperse phase, and Φ' means the volume fraction of the disperse phase in this additional process. Therefore we obtain, for the relation between $\Delta\varepsilon^*$ and $\Delta\Phi'$,

$$\frac{2\varepsilon^* + \varepsilon_p^*}{3\varepsilon^*(\varepsilon^* - \varepsilon_p^*)} \Delta\varepsilon^* = \frac{-\Delta\Phi'}{1-\Phi'}. \quad (63)$$

This mathematical procedure is similar to that employed by Bruggeman,⁹⁾ who derived the equation of the dielectric constant for a concentrated dispersion composed of non-conductive materials.

By succession of these infinitesimally additional processes given by Eq. (63), the system will reach the final concentration Φ and dielectric constant ε^* . Hence we obtain, as a basic equation of ε^* ,

$$\int_{\varepsilon_m^*(C)\varepsilon^*}^{\varepsilon^*} \frac{2\varepsilon^* + \varepsilon_p^*}{3\varepsilon^*(\varepsilon^* - \varepsilon_p^*)} d\varepsilon^* = \int_0^{\Phi} \frac{-d\Phi'}{1-\Phi'} = \log(1-\Phi). \quad (64)$$

† If the volume of the dispersion medium and the disperse phase are denoted by V_m and V_p respectively, the volume fraction Φ' of the disperse phase is given by

$$\Phi' = \frac{V_p}{V_m + V_p}.$$

When a small quantity ΔV_p of the disperse phase is added to the dispersion system, a quantity Φ in Eq. (34) is expressed by

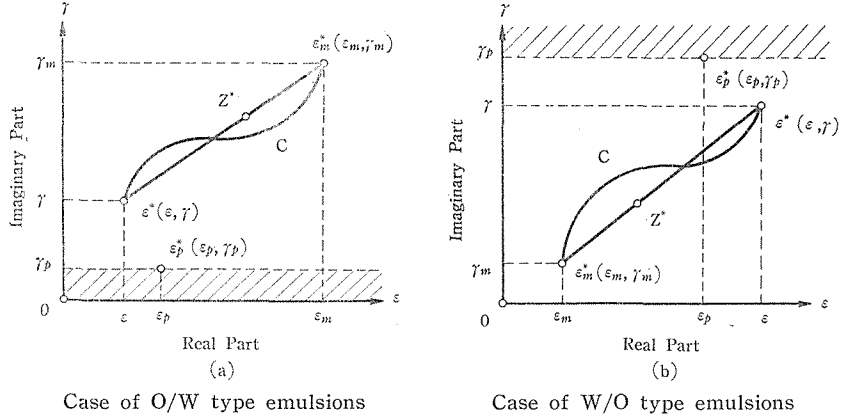
$$\Phi = \frac{\Delta V_p}{(V_m + V_p) + \Delta V_p}.$$

Differentiating Φ' with respect to V_p , we obtain

$$\begin{aligned} \Delta\Phi' &= \frac{\Delta V_p (V_m + V_p) - V_p \Delta V_p}{(V_m + V_p)^2} \\ &= \frac{V_m}{V_m + V_p} \cdot \frac{\Delta V_p}{V_m + V_p} = (1-\Phi')\Phi. \end{aligned}$$

Accordingly

$$\Phi = \frac{\Delta\Phi'}{1-\Phi'}.$$

Fig. 1 Complex plane of the complex dielectric constant ϵ^* .

Let us consider in Fig. 1 a complex plane of ϵ^* , its abscissa and ordinate denoting the real part ϵ and the imaginary part γ respectively. A complex integral of the left side of Eq. (64) is integrated along a certain contour C from ϵ_m^* to ϵ^* in the complex plane shown in Fig. 1.

A contour C is determined by the correlation between ϵ and γ at each stage in a series of successive additions. Hence we can not know a priori an analytical representation of the contour C .

B) Evaluation of the Complex Integral⁽⁶⁾

A function

$$f(\epsilon^*) = \frac{2\epsilon^* + \epsilon_p^*}{3\epsilon^*(\epsilon^* - \epsilon_p^*)} = -\frac{1}{3\epsilon^*} + \frac{1}{\epsilon^* - \epsilon_p^*} \quad (65)$$

has two poles, $\epsilon^* = 0$ and $\epsilon^* = \epsilon_p^*$. One pole $\epsilon^* = 0$ is the origin of the complex plane shown in Fig. 1. Where is the other pole $\epsilon^* = \epsilon_p^*$, is still uncertain.

If we consider the actual cases of emulsions, it may be probable that the conductivity of the dispersion system κ is higher than that of the oil phase, and is lower than that of the water phase. Such physical meanings are expressed, in part, by the following relations:

$$\kappa > \kappa_p > 0 \quad \text{when} \quad \kappa_m > \kappa_p \quad (\text{for the O/W type}) \quad (66)$$

and

$$\kappa_p > \kappa > 0 \quad \text{when} \quad \kappa_p > \kappa_m \quad (\text{for the W/O type}), \quad (67)$$

in other words,

$$\gamma > \gamma_p > 0 \quad \text{when} \quad \gamma_m > \gamma_p \quad (\text{Fig. 1(a), O/W type}) \quad (68)$$

and

$$\gamma_p > \gamma > 0 \quad \text{when} \quad \gamma_p > \gamma_m \quad (\text{Fig. 1(b), W/O type}). \quad (69)$$

On these assumptions, it is shown that there exists no pole of the function $f(\epsilon^*)$ given by Eq. (65) in a certain domain bounded by the contour C and a straight contour $\overrightarrow{\epsilon_m^* \epsilon^*}$ from ϵ_m^* to ϵ^* , the function $f(\epsilon^*)$ being regular in such

domain. Therefore it is proved by the use of Cauchy's theorem¹⁷⁾ that the integral of $f(\varepsilon^*)$ along the contour C is equal to that along the contour $\overrightarrow{\varepsilon_m^* \varepsilon^*}$

Points z^* on the straight contour $\overrightarrow{\varepsilon_m^* \varepsilon^*}$ from ε_m^* to ε^* are given by

$$z_m^* = \varepsilon_m^* + x(\varepsilon^* - \varepsilon_m^*), \quad x[0, 1]. \quad (70)$$

Hence we have

$$dz^* = (\varepsilon^* - \varepsilon_m^*) dx. \quad (71)$$

Thus the complex integral shown in Eq. (64) is easily evaluated as follows:

$$\begin{aligned} \int_{\varepsilon_m^*(C)\varepsilon^*} f(\varepsilon^*) d\varepsilon^* &= \int_{\overrightarrow{\varepsilon_m^* \varepsilon^*}} f(\varepsilon^*) d\varepsilon^* = \int_{\varepsilon_m^*}^{\varepsilon^*} f(z^*) dz^* \\ &= \int_{\varepsilon_m^*}^{\varepsilon^*} \left[-\frac{1}{3z^*} + \frac{1}{z^* - \varepsilon_p^*} \right] dz^* \\ &= \int_0^1 \left[-\frac{1}{3\left(\frac{\varepsilon_m^*}{\varepsilon^* - \varepsilon_m^*} + x\right)} + \frac{1}{\frac{\varepsilon_m^* - \varepsilon_p^*}{\varepsilon^* - \varepsilon_m^*} + x} \right] dx \\ &= -\frac{1}{3} \log \left(\frac{\varepsilon_m^*}{\varepsilon^*} \right) + \log \left(\frac{\varepsilon^* - \varepsilon_p^*}{\varepsilon_m^* - \varepsilon_p^*} \right). \end{aligned} \quad (72)$$

Accordingly we obtain the following equation, which is the Bruggeman equation¹⁸⁾ extended to the complex numbers

$$\frac{\varepsilon^* - \varepsilon_p^*}{\varepsilon_m^* - \varepsilon_p^*} \left(\frac{\varepsilon_m^*}{\varepsilon^*} \right)^{1/3} = 1 - \Phi. \quad (74)$$

Here each factor in Eq. (74) is transformed as

$$\varepsilon^* - \varepsilon_p^* = [(\varepsilon - \varepsilon_p)^2 + (\gamma - \gamma_p)^2]^{1/2} \cdot \exp\left(-j \tan^{-1} \frac{\gamma - \gamma_p}{\varepsilon - \varepsilon_p}\right), \quad (75)$$

$$\varepsilon_m^* - \varepsilon_p^* = [(\varepsilon_m - \varepsilon_p)^2 + (\gamma_m - \gamma_p)^2]^{1/2} \cdot \exp\left(-j \tan^{-1} \frac{\gamma_m - \gamma_p}{\varepsilon_m - \varepsilon_p}\right), \quad (76)$$

$$\varepsilon_m^* = (\varepsilon_m^2 + \gamma_m^2)^{1/2} \cdot \exp\left(-j \tan^{-1} \frac{\gamma_m}{\varepsilon_m}\right) \quad (77)$$

and

$$\varepsilon^* = (\varepsilon^2 + \gamma^2)^{1/2} \cdot \exp\left(-j \tan^{-1} \frac{\gamma}{\varepsilon}\right). \quad (78)$$

Substitution of Eqs. (75), (76), (77) and (78) in Eq. (74) and separation of real and imaginary parts give

$$\frac{[(\varepsilon - \varepsilon_p)^2 + (\gamma - \gamma_p)^2]^{1/2} (\varepsilon_m^2 + \gamma_m^2)^{1/3}}{[(\varepsilon_m - \varepsilon_p)^2 + (\gamma_m - \gamma_p)^2]^{1/2} (\varepsilon^2 + \gamma^2)^{1/3}} = (1 - \Phi)^2 \quad (79)$$

and

$$\tan^{-1} \frac{\varepsilon \gamma_m - \varepsilon_m \gamma}{\varepsilon \varepsilon_m + \gamma \gamma_m} = 3 \tan^{-1} \frac{(\varepsilon - \varepsilon_p)(\gamma_m - \gamma_p) - (\varepsilon_m - \varepsilon_p)(\gamma - \gamma_p)}{(\varepsilon - \varepsilon_p)(\varepsilon_m - \varepsilon_p) + (\gamma - \gamma_p)(\gamma_m - \gamma_p)}. \quad (80)$$

Two Eqs. (79) and (80) are the general conditions to give ε and γ or κ .

Eq. (80) is rewritten in a simplified form:

$$\frac{\frac{\gamma_m}{\varepsilon_m} - \frac{\gamma}{\varepsilon}}{1 + \frac{\gamma_m}{\varepsilon_m} \cdot \frac{\gamma}{\varepsilon}} = \frac{X(3-X^2)}{1-3X^2}, \quad (81)$$

where

$$X = \frac{\frac{\gamma_m - \gamma_p}{\varepsilon_m - \varepsilon_p} - \frac{\gamma - \gamma_p}{\varepsilon - \varepsilon_p}}{1 + \frac{\gamma_m - \gamma_p}{\varepsilon_m - \varepsilon_p} \cdot \frac{\gamma - \gamma_p}{\varepsilon - \varepsilon_p}}. \quad (82)$$

Moreover, Eq. (81) is rearranged as follows:

$$\begin{aligned} & (\varepsilon\gamma_m - \varepsilon_m\gamma) [(\varepsilon - \varepsilon_p)(\varepsilon_m - \varepsilon_p) + (\gamma - \gamma_p)(\gamma_m - \gamma_p)] \\ & \times [\{(\varepsilon - \varepsilon_p)(\varepsilon_m - \varepsilon_p) + (\gamma - \gamma_p)(\gamma_m - \gamma_p)\}^2 - 3\{(\varepsilon - \varepsilon_p)(\gamma_m - \gamma_p) \\ & - (\gamma - \gamma_p)(\varepsilon_m - \varepsilon_p)\}^2] \\ & = (\varepsilon\varepsilon_m + \gamma\gamma_m) [(\varepsilon - \varepsilon_p)(\gamma_m - \gamma_p) - (\gamma - \gamma_p)(\varepsilon_m - \varepsilon_p)] \\ & \times [3\{(\varepsilon - \varepsilon_p)(\varepsilon_m - \varepsilon_p) + (\gamma - \gamma_p)(\gamma_m - \gamma_p)\}^2 - \{(\varepsilon - \varepsilon_p)(\gamma_m - \gamma_p) \\ & - (\gamma - \gamma_p)(\varepsilon_m - \varepsilon_p)\}^2] \end{aligned} \quad (83)$$

C) Approximation for Special Cases

i) Limiting values of ε and κ at high and low frequencies.

From Eqs. (79) and (81), we have the following relations on ε_h , κ_h , ε_l and κ_l respectively, regardless of the emulsion type, O/W and W/O:

At high frequencies ($\omega \rightarrow \infty$, $\varepsilon_m \gg \gamma_m$, $\varepsilon_p \gg \gamma_p$ and $\varepsilon \gg \gamma$.)

$$\frac{\varepsilon_h - \varepsilon_p}{\varepsilon_m - \varepsilon_p} \left(\frac{\varepsilon_m}{\varepsilon_h} \right)^{1/3} = 1 - \Phi. \quad (84)$$

$$\kappa_h \left[\frac{3}{\varepsilon_h - \varepsilon_p} - \frac{1}{\varepsilon_h} \right] = 3 \left[\frac{\kappa_m - \kappa_p}{\varepsilon_m - \varepsilon_p} + \frac{\kappa_p}{\varepsilon_h - \varepsilon_p} \right] - \frac{\kappa_m}{\varepsilon_m}. \quad (85)$$

At low frequencies ($\omega \rightarrow 0$, $\gamma_m \gg \varepsilon_m$, $\gamma_p \gg \varepsilon_p$ and $\gamma \gg \varepsilon$.)

$$\varepsilon_l \left[\frac{3}{\kappa_l - \kappa_p} - \frac{1}{\kappa_l} \right] = 3 \left[\frac{\varepsilon_m - \varepsilon_p}{\kappa_m - \kappa_p} + \frac{\varepsilon_p}{\kappa_l - \kappa_p} \right] - \frac{\varepsilon_m}{\kappa_m}. \quad (86)$$

$$\frac{\kappa_l - \kappa_p}{\kappa_m - \kappa_p} \left(\frac{\kappa_m}{\kappa_l} \right)^{1/3} = 1 - \Phi. \quad (87)$$

Eq. (84) is the same as the Bruggeman equation⁹⁾ of the dielectric constant for a spherical dispersion.

ii) Case $\kappa_m \gg \kappa_p$ (O/W type emulsion)

Here Eqs. (84), (85), (86) and (87) are reduced to

$$\frac{\varepsilon_h - \varepsilon_p}{\varepsilon_m - \varepsilon_p} \left(\frac{\varepsilon_m}{\varepsilon_h} \right)^{1/3} = 1 - \Phi, \quad (88)$$

$$\frac{\kappa_h}{\kappa_m} = \frac{\varepsilon_h(\varepsilon_h - \varepsilon_p)(2\varepsilon_m + \varepsilon_p)}{\varepsilon_m(\varepsilon_m - \varepsilon_p)(2\varepsilon_h + \varepsilon_p)}, \quad (89)$$

$$\varepsilon_l = \frac{\kappa_l[3\varepsilon_p\kappa_m + (2\varepsilon_m - 3\varepsilon_p)\kappa_l]}{\kappa_m(2\kappa_l + \kappa_p)} \quad (90)$$

and

$$\frac{\kappa_l - \kappa_p}{\kappa_m} \left(\frac{\kappa_m}{\kappa_l} \right)^{1/3} = 1 - \Phi. \quad (91)$$

Especially if it is admissible to put $\kappa_l \gg \kappa_p$, Eqs. (90) and (91) are reduced to

$$\frac{2\varepsilon_l - 3\varepsilon_p}{2\varepsilon_m - 3\varepsilon_p} = (1 - \Phi)^{3/2} \quad (92)$$

and

$$\frac{\kappa_l}{\kappa_m} = (1 - \Phi)^{3/2}. \quad (93)$$

iii) Case $\kappa_p \gg \kappa_m$ (W/O type emulsion)

Here Eqs. (84), (85), (86) and (87) are reduced to

$$\frac{\varepsilon_p - \varepsilon_h}{\varepsilon_p - \varepsilon_m} \left(\frac{\varepsilon_m}{\varepsilon_h} \right)^{1/3} = 1 - \Phi, \quad (94)$$

$$\frac{\kappa_h}{\kappa_p} = \frac{3\varepsilon_h(\varepsilon_h - \varepsilon_m)}{(\varepsilon_p + 2\varepsilon_h)(\varepsilon_p - \varepsilon_m)}, \quad (95)$$

$$\varepsilon_l = \varepsilon_m \frac{\kappa_l(\kappa_p - \kappa_l)}{\kappa_m(\kappa_p + 2\kappa_l)} \quad (96)$$

and

$$\frac{\kappa_p - \kappa_l}{\kappa_p} \left(\frac{\kappa_m}{\kappa_l} \right)^{1/3} = 1 - \Phi. \quad (97)$$

Especially if it is admissible to put $\kappa_p \gg \kappa_l$, Eqs. (96) and (97) are reduced to

$$\varepsilon_l = \varepsilon_m \frac{1}{(1 - \Phi)^3} \quad (98)$$

and

$$\frac{\kappa_l}{\kappa_m} = \frac{1}{(1 - \Phi)^3}. \quad (99)$$

5. NUMERICAL CONSIDERATIONS FOR SOME CASES

A) Usual Emulsions

Almost all emulsions used in practice are made from the oil phase having a low conductivity and a low dielectric constant. In this section, the numerical considerations are made for such oil-water emulsions, in which the dielectric constants of the oil and the water phases are taken to be 2.50 and 76.8 (values at 30°C) respectively.

i) Maxwell theory

In Table 1 and in Fig. 2 are shown the theoretical values and curves obtained respectively from Eqs. (26)-(33).

According to the Maxwell theory based on the stratified model, the dielectric properties of the O/W emulsions is the same as those of the W/O type with the same volume fraction of the oil, since no distinctions are made between the continuous medium and the disperse phase of emulsions. Therefore the Maxwell theory is unable to explain the experimental fact that considerable changes in dielectric constants and conductivities take place on phase inversion of emulsions.

It will be noticed from Table 1 and Fig. 2 that both differences between ε_l and ε_h and between κ_h and κ_l are very large at higher concentrations above 90% for the W/O type, whereas these differences are very large at lower concentrations ($\Phi \rightarrow 0$) for the O/W type. Such a theoretical result concerning the O/W type contradicts our experiences remarkably. Thus the Maxwell theory is also of no use to explain the experimental fact that dielectric dispersions due to the interfacial polarization could not be found in O/W emulsions, whereas such dispersions could be observed in W/O emulsions. Moreover ε_h and κ_l given by Eqs. (26), (28), (30) and (32) show no agreement with experimental values of emulsions.

Therefore it is concluded that the Maxwell theory is not valid qualitatively for the interfacial polarization of a spherical dispersion.

Table 1. Dielectric constants and electrical conductivities of the O/W and the W/O emulsions calculated from the Maxwell theory.

O/W emulsion					
Volume fraction of disperse phase Φ	Dielectric constant		Relative conductivity		
	ε_h	ε_l	$\frac{\kappa_h}{\kappa_m}$	$\frac{\kappa_l}{\kappa_p}$	
	by		by		
	Eq. (26)	Eq. (27)	Eq. (29)	Eq. (28)	
0.0	76.80	∞	1.0000	∞	1.0
0.05	30.89	50.00	0.1537	20.00	0.95
0.1	19.34	25.00	0.05705	10.00	0.9
0.15	14.07	16.67	0.02853	6.667	0.85
0.2	11.06	12.50	0.01659	5.000	0.8
0.3	7.745	8.333	0.007119	3.333	0.7
0.4	5.959	6.250	0.003612	2.500	0.6
0.5	4.842	5.000	0.001988	2.000	0.5
0.6	4.078	4.167	0.001128	1.667	0.4
0.7	3.522	3.571	0.0006310	1.429	0.3
0.8	3.100	3.125	0.0003258	1.250	0.2
0.85	2.924	2.941	0.0002175	1.176	0.15
0.9	2.768	2.778	0.0001299	1.111	0.1
0.95	2.627	2.632	0.00005851	1.053	0.05
1.0	2.500	2.500	0.00000000	1.000	0.0
W/O emulsion					
Volume fraction of disperse phase Φ	Dielectric constant		Relative conductivity		
	ε_h	ε_l	$\frac{\kappa_h}{\kappa_p}$	$\frac{\kappa_l}{\kappa_m}$	
	by		by		
	Eq. (30)	Eq. (31)	Eq. (33)	Eq. (32)	

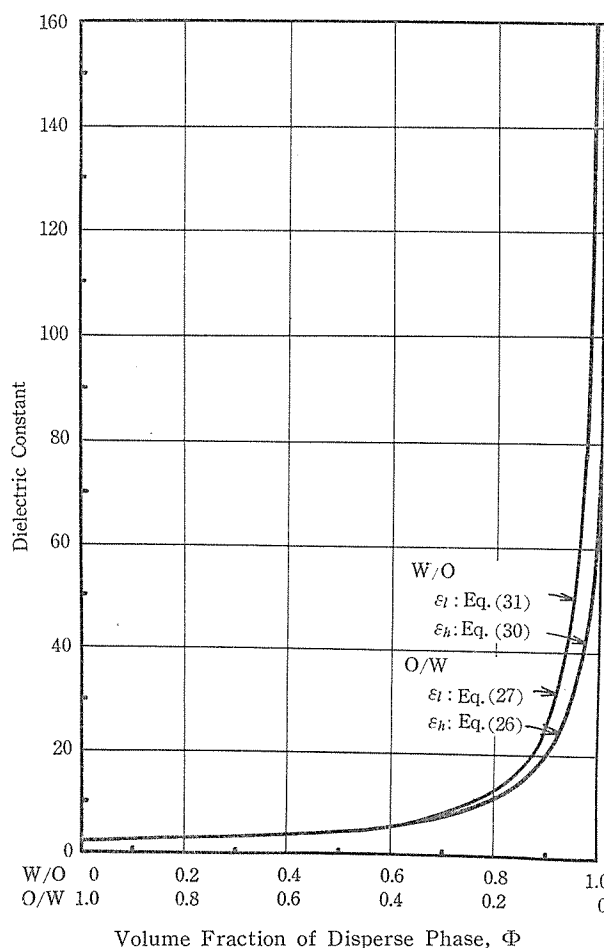


Fig.2. Concentration dependence of dielectric constants ϵ_h and ϵ_l for the O/W and the W/O emulsions given by the Maxwell theory.

ii) Wagner theory

In Tables 2,3 and Fig.3 are shown the theoretical values and curves obtained respectively from Eqs. (55)-(62).

It will be noticed from Tables 2,3 and Fig.3 that both differences between ϵ_l and ϵ_h and between κ_h and κ_l are very small over the whole range of concentration for the O/W type, whereas these differences are very large at higher concentrations of the W/O type. Hence it is expected from the general solution of the Wagner equation that the dispersions of dielectric constants and conductivities are too small to be observed in O/W emulsions and are considerable in W/O emulsions.

In fact, no dielectric dispersion due to the interfacial polarization could be found in O/W emulsions,^{10,11} whereas several workers observed the dielectric dispersions of this type in W/O emulsions as mentioned in the introduction.

Furthermore it is explained from Tables 2,3 and Fig.3 that the considerable

changes of ε_h and κ_i may occur on phase inversion of emulsions.

However it has been recognized in the previous study^{10) 11)} that the observed dielectric constants and conductivities of O/W emulsions do not agree with Eqs. (55) and (57) especially at higher concentrations, and that the observed ε_h of W/O emulsions do not agree with Eq. (59).

Table 2. Dielectric constants and electrical conductivities of the O/W emulsion calculated from the Wagner theory.

Volume fraction of disperse phase Φ	Dielectric constant		Electrical conductivity	
	ε_h	ε_i	$\frac{\kappa_h}{\kappa_m}$	$\frac{\kappa_i}{\kappa_m}$
	by		by	
	Eq. (55)	Eq. (56)	Eq. (58)	Eq. (57)
0.0	76.80	76.80	1.0000	1.0000
0.1	66.33	66.34	0.8572	0.8571
0.2	56.77	56.78	0.7274	0.7273
0.3	48.01	48.02	0.6089	0.6087
0.4	39.95	39.96	0.5002	0.5000
0.5	32.51	32.52	0.4002	0.4000
0.6	25.62	25.63	0.3078	0.3077
0.7	19.22	19.23	0.2223	0.2222
0.8	13.26	13.27	0.1429	0.1429
0.85	10.44	10.44	0.1053	0.1053
0.9	7.702	7.704	0.06900	0.06897
0.95	5.058	5.060	0.03392	0.03390
1.0	2.500	2.500	0.00000	0.00000

Table 3. Dielectric constants and electrical conductivities of the W/O emulsion calculated from the Wagner theory.

Volume fraction of disperse phase Φ	Dielectric constant		Relative conductivity	
	ε_h	ε_i	$\frac{\kappa_h}{\kappa_p}$	$\frac{\kappa_i}{\kappa_m}$
	by		by	
	Eq. (59)	Eq. (60)	Eq. (62)	Eq. (61)
0.0	2.500	2.500	0.000000	1.000
0.1	3.249	3.333	0.001017	1.333
0.2	4.165	4.375	0.002511	1.750
0.3	5.309	5.714	0.004765	2.286
0.4	6.780	7.500	0.008295	3.000
0.5	8.740	10.00	0.01411	4.000
0.6	11.48	13.75	0.02436	5.500
0.7	15.59	20.00	0.04437	8.000
0.8	22.44	32.50	0.09001	13.00
0.85	27.91	45.00	0.1375	18.00
0.9	36.09	70.00	0.2271	28.00
0.95	49.70	145.0	0.4249	58.00
1.0	76.80	∞	1.0000	∞

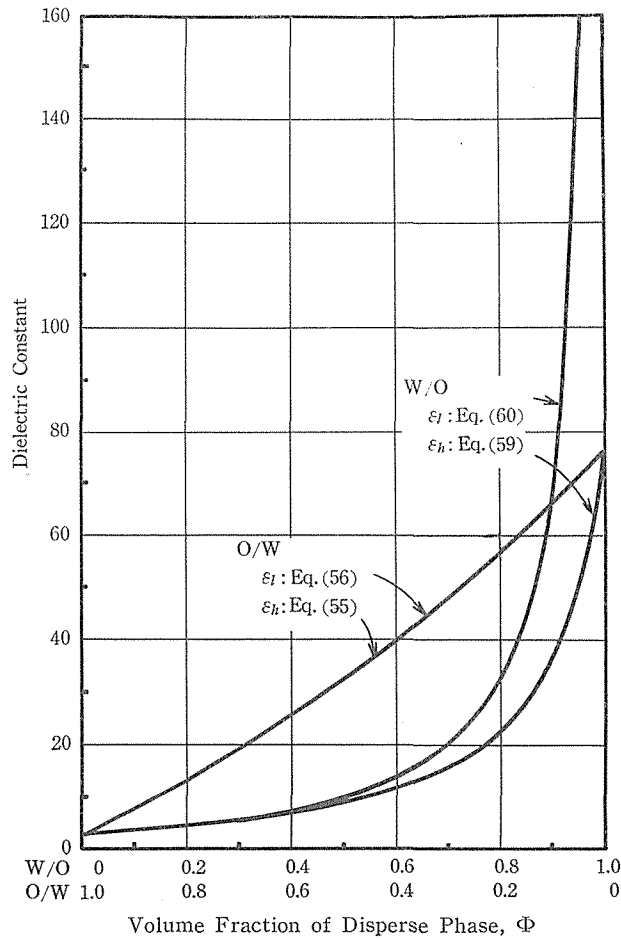


Fig. 3. Concentration dependence of dielectric constants ϵ_h and ϵ_l for the O/W and the W/O emulsions given by the Wagner theory.

Therefore it is concluded that, in the case of usual emulsions of both O/W and W/O type, the Wagner theory is not valid quantitatively for the interfacial polarization of a spherical dispersion.

iii) New theory

In Tables 4, 5 and Fig. 4 are shown the theoretical values and curves obtained respectively by Eqs. (88)–(99).

As is easily known from the assumptions used, Eqs. (92), (93), (98) and (99) do not hold in the vicinity of $\Phi=1$. Since the function $f(\epsilon^*)$ is not regular at $\epsilon^*=\epsilon_p^*$, the results of the present theory are not valid at $\Phi=1$. Hence, in the lowest rows ($\Phi=1$) of Tables 4 and 5 are shown the limiting values given by Eqs. (90), (91), (96) and (97) at higher concentrations ($\Phi \rightarrow 1$).

Tables 4, 5 and Fig. 4 show that O/W emulsions give different dielectric constants and conductivities from those of the W/O type with the same volume fraction of the oil phase. Thus the considerable changes in the dielectric properties on

phase inversion of emulsions can be interpreted by the present theory.

It will be noticed from Tables 4,5 and Fig.4 that both differences between ε_i and ε_h and between κ_h and κ_i are very small over the whole range of concentration for O/W emulsions, whereas these differences are very large at higher concentrations of W/O emulsions. Therefore it is concluded from the present theory

Table 4. Dielectric constants and electrical conductivities of the O/W emulsion calculated from the new theory.

Volume fraction of disperse phase Φ	Dielectric constant		Relative conductivity	
	ε_h	ε_i	$\frac{\kappa_h}{\kappa_m}$	$\frac{\kappa_i}{\kappa_m}$
	by		by	
	Eq. (88)	Eq. (92)	Eq. (89)	Eq. (93)
0.0	76.80	76.80	1.0000	1.0000
0.1	66.11	66.12	0.8539	0.8538
0.2	56.00	56.02	0.7158	0.7155
0.3	46.50	46.54	0.5861	0.5857
0.4	37.65	37.70	0.4654	0.4648
0.5	29.51	29.58	0.3544	0.3536
0.6	22.13	22.23	0.2541	0.2530
0.7	15.60	15.75	0.1659	0.1643
0.8	10.04	10.28	0.09175	0.08944
0.85	7.671	7.994	0.06082	0.05809
0.9	5.605	6.060	0.03473	0.03162
0.95	3.873	4.567	0.01419	0.01118
1.0	2.500	2.500	0.00000	$\sim \kappa_p/\kappa_m$

Table 5. Dielectric constants and electrical conductivities of the W/O emulsion calculated from the new theory.

Volume fraction of disperse phase Φ	Dielectric constant		Relative conductivity	
	ε_h	ε_i	$\frac{\kappa_h}{\kappa_p}$	$\frac{\kappa_i}{\kappa_m}$
	by		by	
	Eq. (94)	Eq. (98)	Eq. (95)	Eq. (99)
0.0	2.500	2.500	0.000000	1.000
0.1	3.317	3.429	0.001312	1.372
0.2	4.499	4.883	0.004231	1.953
0.3	6.242	7.289	0.01056	2.915
0.4	8.852	11.57	0.02402	4.630
0.5	12.79	20.00	0.05190	8.000
0.6	18.69	39.06	0.1070	15.63
0.7	27.33	92.59	0.2084	37.04
0.8	39.51	312.5	0.3789	125.0
0.85	47.14	740.7	0.4966	296.3
0.9	55.87	2500.	0.6386	1000.
0.95	65.75	20000.	0.8062	8000.
1.0	76.80	0.0	1.0000	$\sim \kappa_p/\kappa_m$

Interfacial Polarization for Two-Phase Mixtures

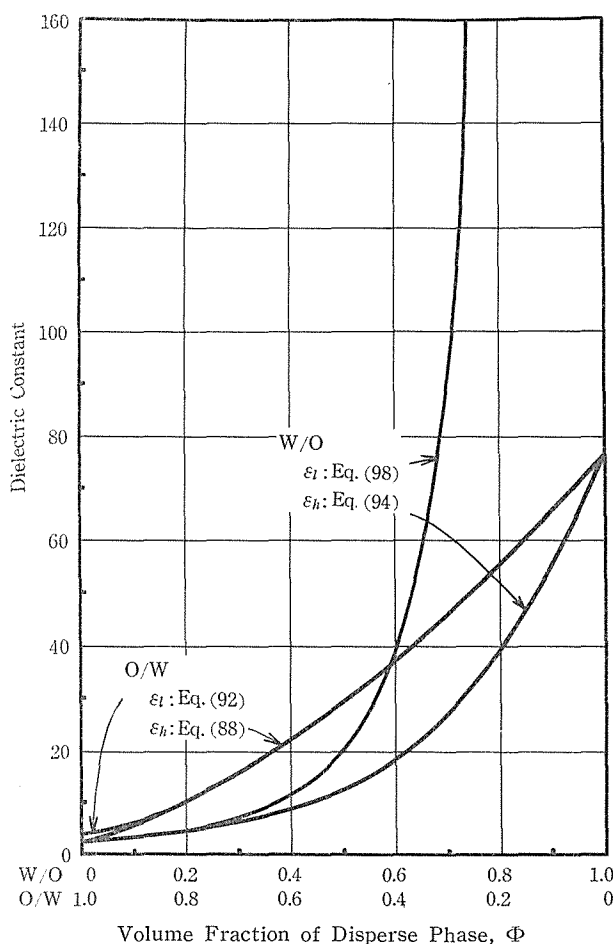


Fig. 4. Concentration dependence of dielectric constants ϵ_h and ϵ_l for the O/W and the W/O emulsions given by the new theory.

that the dispersions of dielectric constants and conductivities are too small to be observed in O/W emulsions and are considerable in W/O emulsions.

Strictly speaking, the differences between ϵ_l and ϵ_h for O/W emulsions are rather appreciable at very high concentrations above 90%, where it may be difficult to prepare actual emulsions.

In the previous dielectric measurements^{10,11)} of O/W emulsions over a wide range of frequency, no dielectric dispersion due to the interfacial polarization could be observed, and the dielectric constants and the conductivities were expressed well by Eqs. (88) and (93) respectively for concentrations up to 85%.

Recently Rue and Tobias¹⁸⁾ have observed conductivities of suspensions of glass beads in ZnBr_2 solutions, concentrations of the disperse phase being less than 40%. It was found from their results that the dependence of the conductivity of random suspensions on volume fraction is expressed better by Eq. (93) rather than by Eq. (57).

In more recent dielectric measurements⁹⁾ of W/O emulsions over a wide range

of frequency, striking dielectric dispersions due to the interfacial polarization were observed in accordance with the prediction from the new theory, the limiting dielectric constants at high frequencies ϵ_h being expressed well by Eq. (94) for concentrations up to 80%.

Therefore it is concluded that, in the case of usual emulsions, the new theory is valid quantitatively for the values of ϵ and κ of O/W emulsions and the values of ϵ_h of W/O emulsions.

B) Nitrobenzene-Water Emulsions

In the preceding section, it was concluded from both the Wagner and the new theory that the differences between ϵ_l and ϵ_h are very small over the whole range of concentration for the usual emulsions of the O/W type. Such a conclusion concerning the differences between ϵ_l and ϵ_h for the O/W emulsions are attributable to the approximate equality between the expression of ϵ_l and that of ϵ_h for smaller values of ϵ_p . Namely, Eq. (56) and Eq. (55) lead to

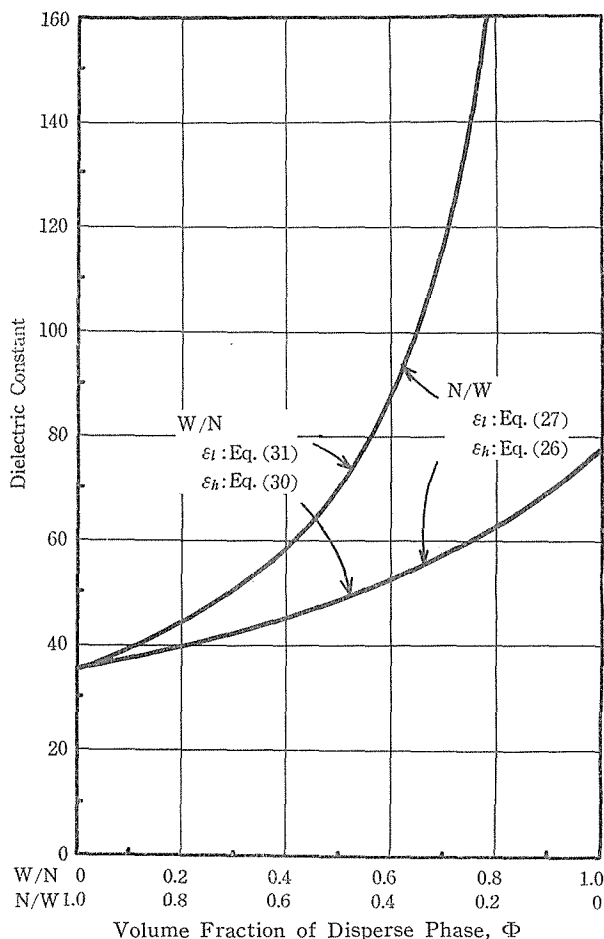


Fig. 5. Concentration dependence of dielectric constants ϵ_h and ϵ_l for the nitrobenzene-in-water and the water-in-nitrobenzene emulsions given by the Maxwell theory.

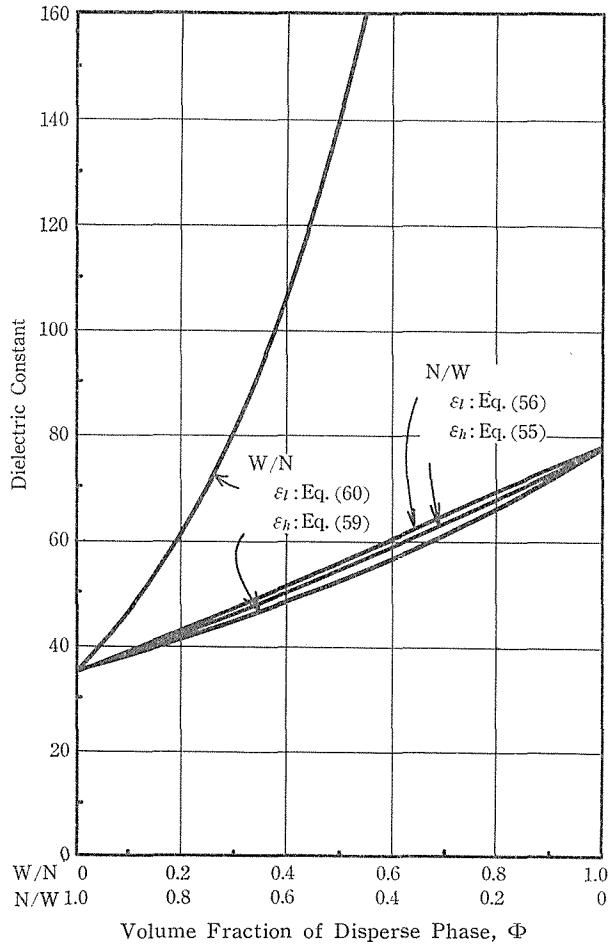


Fig. 6. Concentration dependence of dielectric constants ϵ_h and ϵ_l for the nitrobenzene-in-water and the water-in-nitrobenzene emulsions given by the Wagner theory.

$$\epsilon_l \doteq \epsilon_m \frac{2(1-\Phi)}{2+\Phi} \doteq \epsilon_h, \quad (100)$$

and Eq. (92) and Eq. (88) lead to

$$\epsilon_l \doteq \epsilon_m (1-\Phi)^{3/2} \doteq \epsilon_h, \quad (101)$$

respectively for smaller values of ϵ_p .

Accordingly it is suggested that another conclusion may be drawn for the case of oil phase having a high dielectric constant such as nitrobenzene.

In this section, the numerical considerations are made for emulsions of the nitrobenzene-in-water (N/W) type and the water-in-nitrobenzene (W/N) type, in which the conductivity of water is much higher than that of nitrobenzene, the dielectric constants of nitrobenzene and water being taken to be 35.15 and 78.0 (values at 20°C) respectively.

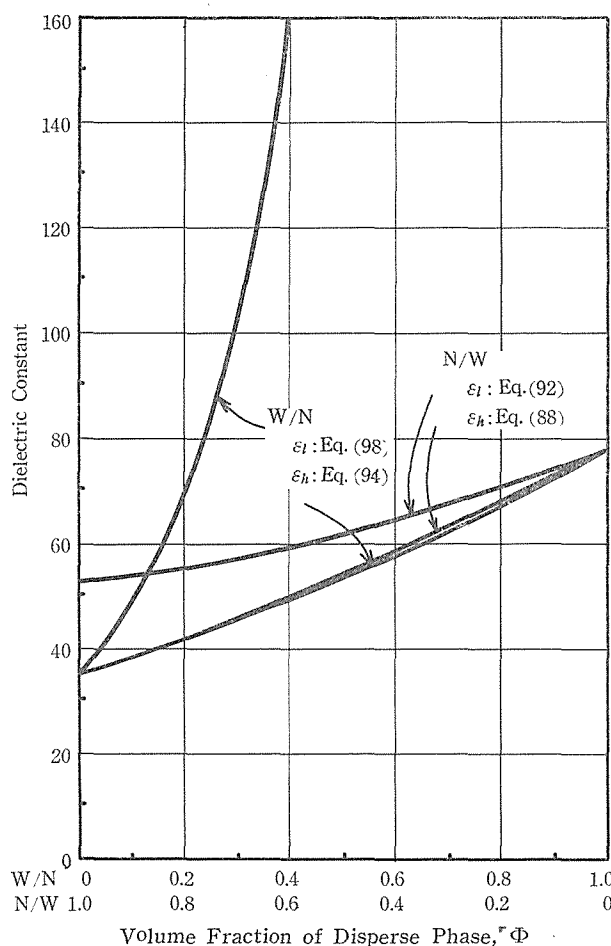


Fig. 7. Concentration dependence of dielectric constants ϵ_h and ϵ_l for the nitrobenzen-in-water and the water-in-nitrobenzene emulsions given by the new theory.

i) Maxwell theory

Fig. 5 shows the theoretical curves of ϵ_h and ϵ_l calculated from Eqs. (26), (27), (30) and (31).

It will be seen that the differences between ϵ_l and ϵ_h are very large for both the N/W and the W/N type. The theoretical result that these differences for the N/W type are very large at lower concentrations ($\Phi \rightarrow 0$), is not valid for the actual emulsions.

ii) Wagner theory

Fig. 6 shows the theoretical curves of ϵ_h and ϵ_l calculated from Eqs. (55), (56), (59) and (60).

It will be seen that the differences between ϵ_l and ϵ_h are very small over the whole range of concentration for the N/W type, whereas these differences are very large for the W/N type. Hence it is expected from the Wagner theory that

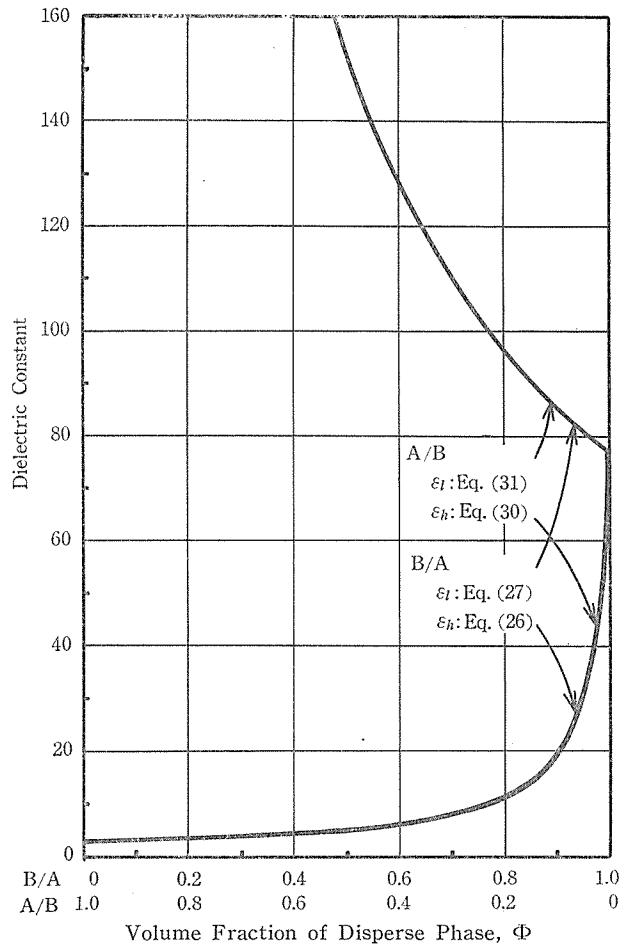


Fig. 8. Concentration dependence of dielectric constants ϵ_h and ϵ_l for the A-in-B and the B-in-A emulsions given by the Maxwell theory.

Phase A: dielectric constant 2.5, high conductivity.

Phase B: dielectric constant 76.8, low conductivity.

the dielectric dispersions are too small to be observed in N/W emulsions and are considerable in W/N emulsions.

According to the dielectric measurements¹⁰⁾ on nitrobenzene-in-water emulsions, striking dielectric dispersions due to the interfacial polarization were observed contrary to the expectation from the Wagner theory.

Therefore it is concluded that the Wagner theory is not valid qualitatively for the interfacial polarization of N/W emulsions.

iii) New theory

Fig. 7 shows the theoretical curves of ϵ_h and ϵ_l calculated from Eqs. (88), (92), (94) and (98).

It will be seen that the differences between ϵ_l and ϵ_h are very large not only for the W/N type but also for the N/W type at higher concentrations. Hence it is expected from the new theory that the dielectric dispersions may be found even

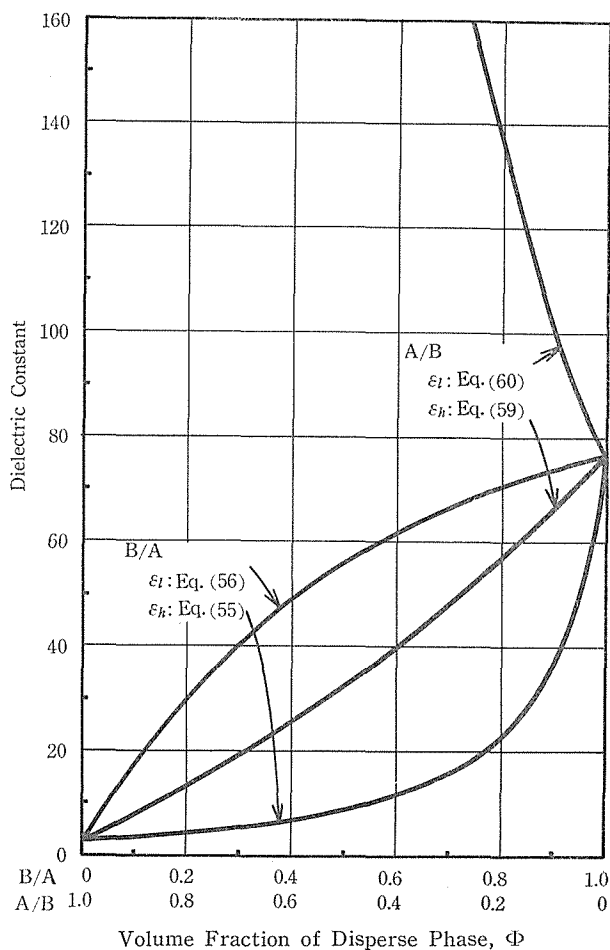


Fig. 9. Concentration dependence of dielectric constants ϵ_h and ϵ_l for the A-in-B and the B-in-A emulsions given by the Wagner theory.
 Phase A: dielectric constant 2.5, high conductivity.
 Phase B: dielectric constant 76.8, low conductivity.

in N/W emulsions, which is a kind of O/W type emulsions.

In the recent dielectric measurements¹⁹⁾ of N/W emulsions, striking dielectric dispersions due to the interfacial polarization were observed in accordance with the prediction from the new theory, the limiting dielectric constants at high frequencies ϵ_h being expressed well by Eq. (88).

Therefore it is concluded that the new theory is valid qualitatively for the interfacial polarization of N/W emulsions.

C) Two-Phase Mixtures of Special Type

As seen from the considerations shown in the foregoing sections, the characteristics of the dielectric dispersion depend strongly on the relationship among dielectric constants and conductivities of the dispersion medium and the disperse phase. This section deals with, in contrast with the case of usual emulsions, the

Interfacial Polarization for Two-Phase Mixtures

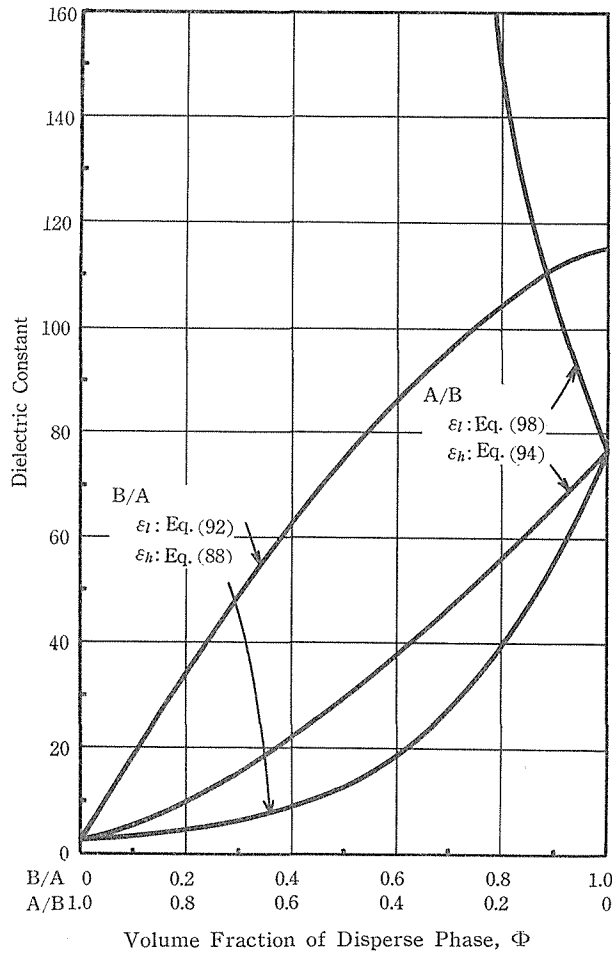


Fig. 10. Concentration dependence of dielectric constants ϵ_h and ϵ_l for the A-in-B and the B-in-A emulsions given by the new theory.
Phase A: dielectric constant 2.5, high conductivity.
Phase B: dielectric constant 76.8, low conductivity.

special mixtures composed of two phases, one (Phase A) having both a low dielectric constant and a high conductivity, the other (Phase B) having both a high dielectric constant and a low conductivity.

Fig. 8, 9 and 10 show the theoretical curves of ϵ_h and ϵ_l calculated from the Maxwell, the Wagner and the new theory respectively. As regards the numerical calculations of ϵ_h and ϵ_l , approximate relations for the case of $\kappa_p \gg \kappa_m$ are applied to the A/B type, and those for the case of $\kappa_m \gg \kappa_p$ are applied to the B/A type, in which the dielectric constants of the phase A and the phase B are taken to be 2.5 and 76.8 respectively.

Considerable differences between ϵ_l and ϵ_h are found in each of Fig. 8, 9 and 10. Hence the pronounced dielectric dispersions are expected from each theory. It is hoped to examine the validity of these theoretical predictions in the light of results observed in a variety of two-phase mixtures.

6. CONCLUSIONS

The general solutions of the Maxwell and the Wagner theory were derived, the dielectric dispersions being found to be characterized by single relaxation time. The general solution of the new theory are not obtained yet, the type of the dielectric dispersion being unknown.

Table 6 summarizes the results of theoretical considerations.

The Maxwell theory is of no use for the dispersion systems composed of the continuous medium and the disperse phase, though this theory may be valid for the two-phase mixtures in a stratified structure. The Wagner theory is valid qualitatively for the usual emulsions, being of no use for nitrobenzene-in-water emulsions. The new theory is valid not only for the usual emulsions but also for nitrobenzene-in-water emulsions.

Table 6. Comparison of the theories on the interfacial polarization for two-phase mixtures.

	Maxwell theory	Wagner theory	New theory
General expression	Eq. (4)	Eq. (34)	Eq. (74)
Expression of ϵ_h	Wiener's <i>Grenzformel</i>	Wiener's equation	Bruggeman's equation
Model of the heterogeneous structure	Stratified structure	Dilute dispersion of spherical particles	Concentrated dispersion of spherical particles
Distinction between the continuous medium and the disperse phase	No	Yes	Yes
Change in dielectric properties on phase inversion	No	Yes	Yes
Type of the dielectric dispersion	Single relaxation	Single relaxation	Unknown
Condition necessary for the dielectric dispersion	$\epsilon_m \kappa_p \neq \epsilon_p \kappa_m$	$\epsilon_m \kappa_p \neq \epsilon_p \kappa_m$	Unknown
Dielectric dispersion in usual emulsions			
O/W	Pronounced at lower concentrations	Negligibly small	Negligibly small
W/O	Pronounced at higher concentrations	Pronounced	Pronounced
in nitrobenzene-water emulsions			
N/W	Pronounced	Very small	Pronounced
W/N	Pronounced	Pronounced	Pronounced
in two-phase mixture of a special type			
A/B	Pronounced	Pronounced	Pronounced
B/A	Pronounced	Pronounced	Pronounced

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